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Treatment of paper wastewater by palm kernel shell-based activated carbon adsorption

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ABSTRACT

In this study, removal rates of phenol which causes toxic and impurities were investigated in the paper industry wastewaters using the adsorption technique. Palm shell activated carbon (PSAC) was used as adsorbent in the all experiments. Variables such as the contact time, the dose of adsorbent was chosen as the parameter. In the result of experiments, pH 6, an hour's time and 3 g/L adsorbent dose were found to be suitable for optimum removal. In these circumstances, removal was obtained in 70.58 % rate of phenol. The obtained experimental data were described with a linear regression model. In addition, when specifying explained both Langmuir model of phenol adsorption process with isotherm studies, I. order kinetic model showed that a better fit II. order kinetic model for PSAC of phenol adsorption event with kinetic studies

1. INTRODUCTION

The increase in population has led to the proliferation of industrial enterprises established to meet human needs. This situation has also led to the pollution of environmental media such as air, water, and land. The paper industry is one of these industries. The very high amount of water used during paper production and the fact that it contains organic and inorganic pollutants that are difficult to decompose biologically have made these industries institutions that require more attention environmentally. In order to meet the needs with limited water resources, it is necessary to protect water resources from all kinds of pollution, to recover and reuse wastewater [1]

Phenol is a substance that ranks 11th among the 126 most toxic chemicals (thesis reference). Even if it is found in waters at ppm levels, it causes a significant change in taste and odor during chlorination. In addition, it is an extremely harmful substance for human and animal health. Today, one of the most important water pollution problems is the transformation of aquatic life into a toxic state and thus the unusable state of usable water resources as a result of the discharge of wastewater containing organic and inorganic substances that have toxic effects on human health and the environment into the receiving environment. The sources of phenol, which is a toxic organic compound, are primarily industries such as

petroleum refineries, chemical and plastics industries, and domestic wastewaters. However, phenol is also found naturally in waters. Phenols, which have toxic effects, cause a decrease in the dissolved oxygen concentration in water resources and thus worsen aquatic life conditions. In addition, since they react with chlorine and form chloro-phenol compounds and cause undesirable taste and odor in drinking waters, they must be made compliant with the specified standards in water and wastewater [2].

Adsorption is one of the methods used to remove phenol, which is found in undesirable concentrations in the wastewaters of petroleum refineries, coke, pharmaceutical, paint, plastic, pesticide, and paper industries. The selection and amounts of adsorbents to be used in this method are a very important factor in terms of both treatment efficiency and cost [2]. Most of the adsorption studies that have yielded the desired results so far are studies conducted with activated carbon. Activated carbon has a large surface area, is an expensive adsorbent, and is quite difficult to obtain. For this reason, research has been conducted on alternative adsorbents that are cheap, easy to obtain, and have high adsorption capacity in wastewater treatment. Palm shell-based activated carbon is one of these alternatives [2].

In general, the treatment of industrial wastewaters is difficult and often requires special treatment. The paper industry is one of these

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industries, which is one of the industries that uses the most water and therefore produces a very high amount of wastewater. This industry has also been the subject of much research recently due to the difficult decomposition of some organic substances in the wastewater it produces. Due to this feature, special approaches are applied in wastewater treatment. As is known, the main raw material of paper is cellulose, which is obtained from wood, but recently, paper production from recycled waste paper has also started to gain importance. Since the 1950s, industrialization has been developing at a great speed, and in parallel, large amounts and varieties of chemicals are released into the environment every day. These chemicals, which enter the environment directly, bring many problems with them. Today, these industrial-sourced chemicals are at the forefront of the problems related to the aquatic ecosystem [2].

The paper industry ranks first in industrial water use among all other industrial branches, third in the release of toxic chemicals into the environment, and fourth in terms of air emissions that impair human health through respiration. Similarly, there is also a very large amount of energy consumption in the paper industry. 7600 kWh of electrical energy is consumed during the production of one ton of paper. 2.4 tons of wood and 440 tons of water are required during the production of one ton of paper. If production is made from paper by recycling instead of wood, 1.2 tons of used paper, 1.2 tons of water, and 2800 kWh of electrical energy are required. If 1 ton of used paper is recovered instead of being thrown into the trash, the cutting of 17 mature pine trees, the release of 36 tons of greenhouse gas CO₂ into the atmosphere, the waste of 4100 kWh of electrical energy, the release of 267 kg of polluting gas into the atmosphere, the waste of 1750 liters of fuel oil, the waste of 3-4 m³ of storage space, the destruction of 85 m² of forest area, and the waste of 38.8 tons of water are prevented [3]. The paper industry is an industrial sector that includes the stages from the production of cellulose, wood pulp, and waste paper pulp from wood, annual plants, and waste paper raw materials to the conversion of these intermediate products into paper by various means.

In recent years, the increase in pollution caused by industrial wastes and their disposal has become an extremely important environmental problem. In particular, the treatment of industrial wastewaters in a way that does not harm the environment has gained importance. Various chemicals are used in many industries such as paper, leather, food, and cosmetics. These chemicals used cause color changes in wastewater and adversely affect the environment and human health.

The treatment of paper industry wastewaters is quite difficult. This is because the materials used during production have different structures and the wastewater flow rate is very high [4]. Chlorine is

used as a bleaching agent in the bleaching of paper pulp. Due to excessive chlorine use, chlorine-rich phenolic and lignin compounds are present in wastewaters. These wastewaters are colored, and it is thought that the color is caused by lignin and functional groups on the molecule. A large part of phenolic compounds also originates from the lignin system. Chlorinated phenolic and lignin compounds cause excessive environmental pollution and especially form chloroform, which is carcinogenic in wastewaters. In the literature studies, it is reported that 12 types of phenolic compounds are present in this type of wastewater [5]. Due to the incomplete removal and toxicity of these chlorinated organics in treatment plants, some restrictions are imposed on their use. Although many countries have imposed restrictions on the discharge of this type of wastewater into the environment, no restrictions have yet been imposed in our country [6].

In this study, phenol removal rates in paper wastewaters were investigated using palm shell-based activated carbon as an adsorbent. Although there are many studies in the literature on the treatment of paper industry wastewaters by biological methods, very few studies have been found using the direct adsorption method. Considering this deficiency, in our country where the phenomenon of environmental pollution is gaining importance, it is aimed to make the adsorption method usable in the cleaning of wastewaters in terms of both economy and efficiency, and to bring palm shell-based activated carbon into the economy in a different way.

2. METHOD

2.1. Channel Systems and Investigation of These Systems

In the studies conducted, the removal of phenol pollutant by palm shell-based activated carbon adsorption from paper industry wastewater was investigated. In all experimental studies carried out for this purpose, operating parameters were tried to be determined based on the batch reactor model. By utilizing the data obtained after the experiments, it was aimed to optimize the variable parameters. The point focused on in the evaluation of the obtained experimental results was to determine the appropriate conditions that provide the maximum adsorption capacity where the phenol concentration in the paper industry wastewater decreased compared to the initial concentration after the experiments performed under a certain operating parameter. The wastewater sample used in the experimental studies was taken from a paper production facility in Konya. In the analyses performed according to standard methods, the total phenol content of the paper wastewater used in all studies was measured as 0.85 mg/L, the COD value was 604 mg/L, and the pH value was 6 (Table 1).

- pH Meter: pH values were measured with a Hana Instruments brand HI 9321 microprocessor model portable pH meter.

- Spectrophotometer: YSI 9500 (USA) 9500 set brand, a device suitable for field type, water, sea water, wastewater analysis measurements, with kits, capable of measuring phenol in the range of 0-5 mg/L.

- Orbital Incubator: A Gallenkamp brand orbital incubator with time control, adjustable internal temperature from minimum 4 °C to maximum 60 °C, and a shaking range of 0~400 rpm was used.

- Precision Balance: A Presica brand XB 220A model precision balance with a measurement range of 0.0001–220 g was used.

- Pure Water Device: Nüve brand NS 112 model pure water device. Distillation unit is

available. It has a capacity to produce approximately 15 L of pure water per hour.

- Peristaltic Pump: Longer Pump BT 100-1J model peristaltic pump was used. The pump operates in the speed range of 1-100 rpm.

2.2. Adsorbent

The palm shell-based activated carbon used in this study was obtained from KD Technology SND BHD, a local manufacturer in Malaysia. In the experiments, palm shell-based activated carbon passed through a 0.5 mm pore size sieve was used. No pretreatment was applied. The adsorbent was then kept in an oven at 50°C for 1 h and stored in a desiccator throughout the experiments. The physicochemical properties of palm shell-based activated carbon are given in Table 2.

Table 1. Characteristic Properties of Used Paper Wastewater

Component	Phenol	KOI	pH
Amount of substance	0.85 mg/L	604 mg/L	6

Table 2. Physicochemical Properties of Palm Kernel Shell-Based Activated Carbon*

Parameter	Values	Test Method
Iodine number (mg/g)	1150	ASTM D4607-94
Physical Hardness (%)	88-96	ASTM D3802-79
Butane Activity (%)	20-30	ASTM D5742-95
CCL ₄ Aktiviti (%)	55-77	ASTM D3467-94
Ash content (%)	5	ASTM D2866-94
Moisture (%)	5	ASTM D2867-95
pH	9-11	ASTM D3838-94
Surface area (m ² /g)	950-1000	BET N ₂
Density (g/L)	420-520	ASTM D2854-96

* KD Tecnology SND BHD technical data

2.3. Adsorption Experiments

Adsorption experiments were carried out using batch operation conditions. Determined amounts of adsorbent and 100 ml of paper industry wastewater were taken into 250 ml glass Erlenmeyer flasks, and the mouths were closed and mixed in an orbital shaker. At the end of the contact time, the samples were filtered through 0.45 µm (milipore) pore size filters, and phenol measurement was performed in the filtered water using a spectrophotometer and three-stage tablet phenol kits.

2.4. Effect of Contact Time

The impact of contact time was studied by adding 3 g/L palm shell-based activated carbon to 100 mL of wastewater sample with an initial phenol concentration of 0.85 mg/L and a pH of 6. The mixture was stirred at 200 rpm and 25 °C for various time intervals (0-10-20-40-60-75 minutes). After agitation, samples were filtered through 0.45 µm

pore-sized filters, and phenol concentrations were determined in the filtered water using a spectrophotometer and three-stage tablet phenol kits. For each contact time, the outlet concentration was determined, and the adsorption capacities were calculated using the following equation:

$$q_e = (C_0 - C_e) * v/M \quad (1)$$

where, q_e is defined as the concentration adsorbed onto PKAK (mg/g), M is the weight of the adsorbent used (g), v is the wastewater volume (L), C_0 is the inlet concentration (mg/L), and C_e is the equilibrium concentration (mg/L) [7]. When the adsorption capacity (q_e) was at its highest, other adsorption experiments were continued. Three-stage phenol measurements were performed using a YSI 9500 wastewater analysis spectrophotometer.

2.5. Effect of pH

To determine the effect of pH, studies were carried out at pH values ranging from 2 to 12. In this study, 3 g/L palm kernel shell-based activated carbon was added to 100 ml of wastewater with an initial phenol concentration of 0.85 mg/L, and the mixture was stirred at 25 °C. Stirring was performed at 200 rpm for 1 hour. At the end of the period, the samples were filtered through 0.45 µm pore size filters, and phenol measurement was performed in the filtered water using a spectrophotometer and three-stage tablet phenol kits. pH adjustments were carried out using 1M H₂SO₄ and NaOH solutions. Images of the paper wastewater samples filtered and adsorbed with palm kernel shell-based activated carbon as a result of applying different pH values.

2.6. Effect of Adsorbent Dosage

To determine the effect of adsorbent dosage, analyses were carried out by adding palm kernel shell-based activated carbon in different adsorbent amounts (3-6-9-12-15-18-20 g/L) to 100 ml of wastewater sample with an initial phenol value of 0.85 mg/L and a pH value of 6. In the experimental study, the optimum contact time determined for the adsorbent was 60 minutes and the optimum pH was 6. Stirring was performed in an orbital incubator at 25 °C at 200 rpm. At the end of the period, the samples were filtered through 0.45 µm pore size filters, and phenol measurement was performed in the filtered water using a spectrophotometer and three-stage tablet phenol kits. The adsorbent amount with the highest removal efficiency was determined as the optimum dose. Images of the paper wastewater sample before and after the palm kernel shell-based activated carbon adsorption process.

2.7. Isotherm Studies

In order to determine the effect of the initial adsorbent weight change on the phenol adsorption of the adsorbent, the data obtained at equilibrium were confirmed with Langmuir and Freundlich isotherms. Isotherm data were obtained by changing the concentration while the phenol concentration was constant. The accuracy of the Langmuir and Freundlich isotherms was investigated from the values obtained by plotting $1/q_e$ and $1/C_e$ values. Langmuir and Freundlich constants obtained from the slope and intersection points of the graph were determined.

2.8. Kinetic Experiments

Adsorption kinetic experiments were carried out by adding 3 g/L palm kernel shell-based activated carbon, which was accepted as the optimum dose, to paper industry wastewater with a phenol concentration of 0.85 mg/L adjusted with H₂SO₄ solution with a pH value of 2. The adsorbent

and wastewater mixture was stirred at 200 rpm for 0-10-20-40-60-75 minutes, respectively, at different temperatures (20-25-30-35-40°C) and for palm kernel shell-based activated carbon adsorption at each temperature. At the end of the period, the samples were filtered through 0.45 µm pore size filters, and phenol measurement was performed in the filtered water using a spectrophotometer and three-stage tablet phenol kits.

To investigate the mechanism of the adsorption process, such as mass transfer and chemical reaction, a suitable kinetic model is needed. Most models, such as the homogeneous surface diffusion model, pore diffusion model, and heterogeneous diffusion model, are applied in batch studies to describe the transfer of adsorbates into the adsorbent particles. Adsorption kinetics describes the rate at which the contaminant in the solution is captured by the adsorbent. The hydraulic retention time in the process depends on the kinetic data [8].

In the study, the adsorption kinetics of palm kernel shell-based activated carbon with phenol were revealed. For this purpose, adsorbents were added at their optimum doses into solutions containing phenol at a concentration of 0.85 mg/L. Adsorption processes were carried out by providing optimum conditions. Palm kernel shell-based activated carbon as an adsorbent was tested separately in paper industry wastewater samples. The obtained data were analyzed by linear analyses. The linear kinetic calculations of the I. and II. degree reactions for palm kernel shell-based activated carbon adsorption are given below.

2.9. Effect of Initial Temperature on Reaction Kinetics

Temperature has two effects on adsorption processes: (i) increased temperature increases the diffusion rate of the adsorbate from one end of the outer boundary layer to the other and in the inner pores of the adsorbent particles because it reduces the viscosity of liquids, (ii) temperature affects the equilibrium capacity of the adsorbent depending on whether the interaction between the adsorbate and the adsorbent is endothermic or exothermic [9]. Temperature is an important parameter in adsorption reactions. According to the adsorption theory, adsorption decreases as a result of increasing temperature and the molecules adsorbed on the adsorbent surface tend to desorb from the surface at rising temperatures [10].

In this study, analyses were carried out at 20, 25, 30, 35 and 40°C by providing optimum conditions in order to determine the effect of temperature on reaction kinetics during kinetic processes. Palm kernel shell-based activated carbon was applied separately to paper wastewater samples. 3 g/L adsorbent was added to 100 ml of paper wastewater, and the shaking process was carried out at 200 rpm for the determined optimum contact time (60 min), then filtered through 0.45 µm

(milipore) pore size filters, and phenol measurement was performed in the filtered water using a spectrophotometer and three-stage tablet phenol kits.

3. RESULTS

The amounts of adsorbed organic matter (phenol) versus contact time are given in Figure 1 for palm kernel shell-based activated carbon. The results showed that the palm kernel shell-based activated carbon adsorption time was suitable for 60 minutes. As seen in Figure 1, adsorption with palm kernel shell-based activated carbon takes place rapidly in the first periods, slows down after about 60 minutes and then remains constant. The maximum adsorption capacity at equilibrium time is 200 mg/g. Sreelatha et al. [11] found that the appropriate contact time for the adsorption process was 60 minutes in their study on dye removal with palm kernel shell-based activated carbon in textile industry wastewater. Similarly, they found that the optimum contact time for the removal of copper, nickel and lead by adsorption with palm kernel shell-based activated carbon was 30 minutes for lead and 75 minutes for copper and nickel [12].

3.1. Effect of pH

The initial pH of the adsorption medium is one of the most important parameters affecting the adsorption process. Figure 2 shows the effect of pH on organic matter adsorption. When the pH changes from 2 to 12, the adsorption capacities change from 186 mg/g to 143 mg/g.

Lim et al. [13] worked at pH=5, the natural value of wastewater, in the removal of endosulfan from industrial wastewaters with palm kernel shell-based activated carbon. Similarly, in a study on the adsorption of 2,4-dichlorophenol from paper industry wastewater with activated carbon, they worked at values varying in the pH range (2-11). They found that adsorption increased under acidic

conditions where the pH value was low, but since there was no very high change, they worked at pH=7, the natural pH value of wastewater. Achak et al. [14] conducted a study on phenol removal from wastewater with banana peel, in which 100 ml of olive industry wastewater was treated with banana peel at 30 °C and 200 rpm for 24 hours, and the pH effect was investigated. They analyzed that the best adsorption capacity occurred at pH 5 and remained constant at higher pH values. Similarly, in a study conducted for phenol removal from wastewater using thermal power plant fly ash, the change in pH values was observed with an optimum contact time of 3 hours. While the optimum pH value for powdered activated carbon was found to be 6, the optimum pH conditions were provided for 5 when thermal power plant ash was used as an adsorbent [15].

3.2. Effect of Adsorbent Dosage

When the adsorbent amount was increased from 3 g/L to 20 g/L, the equilibrium adsorption amount, q_e , decreased from 203 mg/g to 24 mg/g in palm kernel shell-based activated carbon.

It is seen that the q_e value is 203 mg/g when the adsorbent amount is 3 g/L and starts to decrease at higher adsorbent amounts (Figure 3). This situation arises from the establishment of an equilibrium between the unadsorbed molecules in the wastewater and the molecules bound to the adsorbent [14]. For this reason, the optimum adsorbent amount was determined as 3 g/L. In addition, it was observed that filter clogging and interference in experiments occurred at higher adsorbent doses. Sreelatha [11] found that the optimum adsorbent amount for dye removal from textile industry wastewaters with palm kernel shell-based activated carbon was 1.8 g/L and reported that the adsorbed amount remained almost constant when higher amounts of adsorbent were added.

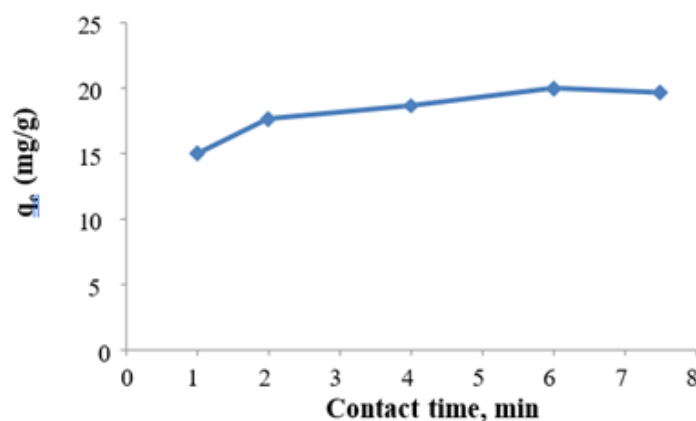


Figure 1. Effect of contact time on organic matter adsorption by PKAK (Adsorbent amount: 3 g/L, pH: 6, T: 25°C)

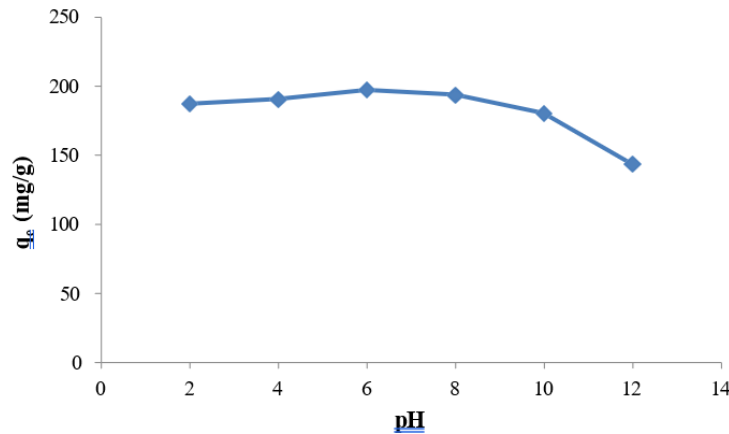


Figure 2. Effect of pH on organic matter adsorption by PKAK (Adsorbent amount: 3 g/L, shaking time 60 min at 200 rpm, T: 25°C)

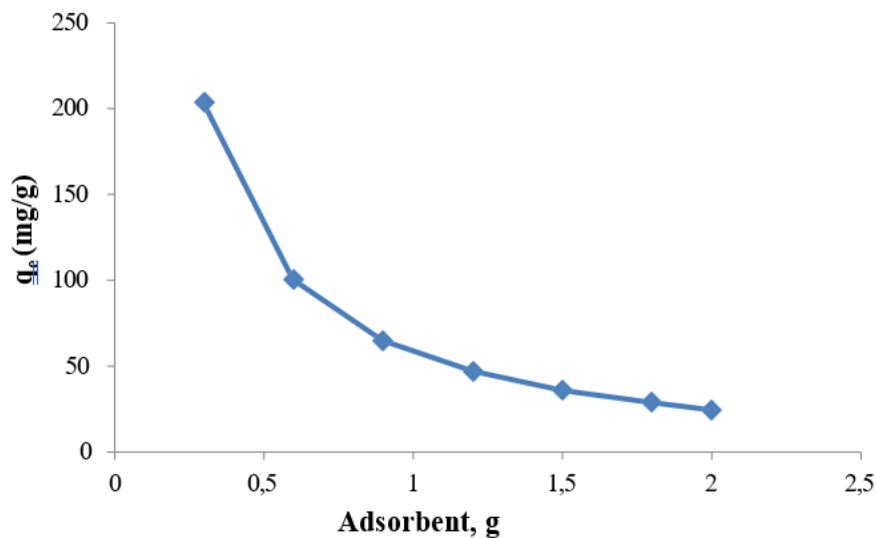


Figure 3. Effect of adsorbent amount on organic matter adsorption by PKAK (pH: 6, shaking time: 60 min at 200 rpm, T: 25°C)

3.3. Pseudo I. and II. Order Kinetic Constants

The highest data were provided at 30°C. The reason for this may be the weakening of the interaction between the adsorbent surface and the adsorbate and the decrease in adsorption as a result of the increase in temperature. Therefore, adsorption can be considered exothermic.

The optimum temperature was determined as 30°C. The decrease in adsorption with increasing temperature indicates a weak adsorption interaction between the metal ions and the adsorbent surface, where the physically occurring adsorption event (physisorption) gains weight. Pseudo I. and II. order kinetic constants determined by linear regression analysis of PKAK adsorption are given in Table 3.

3.4. Isotherm Studies

The importance of isotherms is to determine the equilibrium distribution depending on the concentration between the solution and the

adsorbent (metal ion) against the adsorbent under certain conditions [9].

The data obtained at equilibrium were confirmed with Langmuir and Freundlich isotherms. Isotherm data were obtained by changing the concentration of 's while the phenol concentration was constant. The accuracy of the Langmuir isotherm was investigated from the values obtained by plotting $1/q_e$ and $1/C_e$ values (Figures 4 and 5). Langmuir constants obtained from the slope and intersection points of the graph are also given in Table 4.

The linear method specifies the slope and intercept with a linear trend line that predicts the best Y value for X values. In the kinetic study of phenol removal with palm kernel shell-based activated carbon, it is seen that the pseudo-first-order reaction kinetics fits slightly better than the second-order reaction kinetic model.

Sreelatha [11] reported that the first-order reaction kinetic model fits better than the second-order reaction kinetic model in her kinetic study on

dye removal from textile industry wastewaters with palm kernel shell-based activated carbon. Din [16] reported that the kinetic data fit better with the first-order reaction kinetic model than the second-order reaction kinetic model in his study on phenol removal from synthetic wastewaters with coconut shell-based activated carbon. Achak et al. [14] found

that the correlation coefficient calculated for pseudo-second-order was higher than the correlation coefficient calculated for pseudo-first-order in their study on phenol adsorption with banana peel from olive industry wastewaters, and stated that the pseudo-second-order kinetic model fits phenol adsorption with banana peel.

Table 3. Pseudo I. and II. order kinetic constants determined by linear regression analysis of PKAK adsorption (k_1 : min⁻¹, k_2 : g/mg.min, q_e : mg/g)

T, °C	Experimental, q_e	Pseudo I. degree			Pseudo II. degree		
		k_1	q_e	R^2	k_2	q_e	R^2
20	191.4	0.044	124.18	0.9031	0.0060	90.08	0.9184
25	195.6	0.032	109.47	0.9449	0.0068	93.03	0.9384
30	202.1	0.057	101.24	0.9633	0.0018	106.12	0.9028
35	201.8	0.093	122.35	0.9554	0.0016	112.18	0.9486
40	177.5	0.066	114.86	0.9802	0.0019	111.64	0.9421

Table 4. Izoterm paremeters

Parametre	Langmuir İzotermi	Freundlich İzotermi
q_m (mg/g)	101.3	
K	0.013	26.12
n		1.6
R^2	0.9949	0.9915

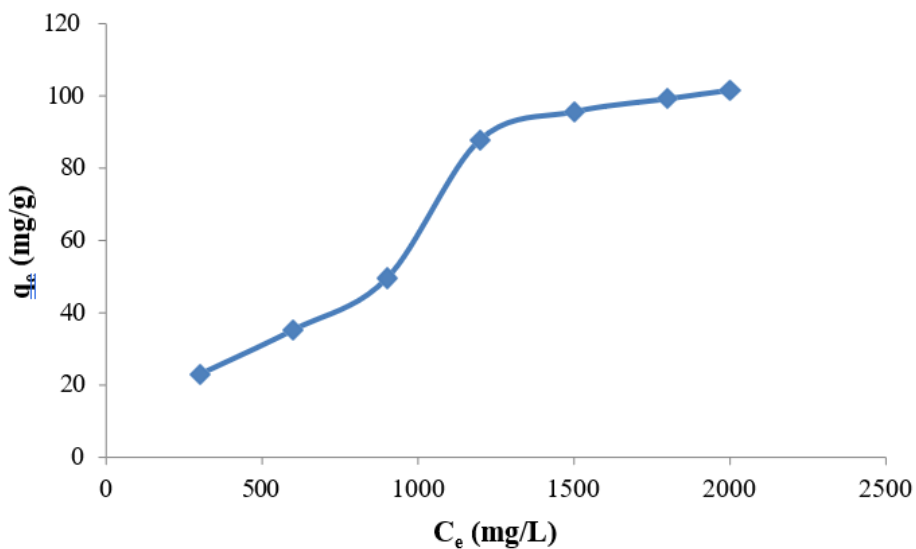


Figure 4. Langmuir isotherm of phenol adsorption of PKAK (Phenol concentration: 0.85 mg/L, pH: 6, stirring speed: 200 rpm, T: 25°C)

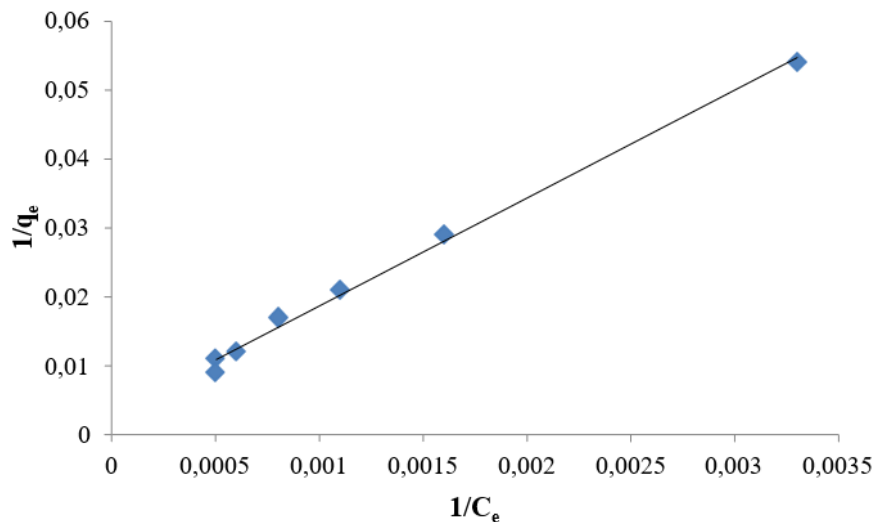


Figure 5. Langmuir isotherm curve (Phenol concentration: 0.85 mg/L, pH: 6, stirring speed: 200 rpm, T: 25°C)

Researchers have stated that the pseudo-second-order kinetic model has a better correlation with experimental kinetic data if the reaction rate is controlled by chemical change [17]. Therefore, for linear solution, it can be said that the pseudo-first and second-order kinetic model provides a good correlation for phenol adsorption with palm kernel shell-based activated carbon. However, it is seen that the pseudo-first-order kinetic model has a better correlation with experimental kinetic data and has a higher value than the correlation coefficient calculated for pseudo-second-order.

Langmuir isotherm is based on the assumption that the adsorption surface is held as a single layer by metal ions and that there is no subsequent interaction between the adsorbed molecules. Therefore, adsorption reaches saturation and does not occur further [18]. Ku et al. [19], in their study on the adsorption of phenols (2-chlorophenol, 2,4-dichlorophenol, 2, 4, 6-trichlorophenol, 2-nitrophenol, 2, 4-dinitrophenol, 2-methylphenol and 2, 4-dimethylphenol) from aqueous solutions with polystyrene divinylbenzene resin adsorption, found that the adsorption of phenols onto XAD-4 resin was compatible with both Langmuir and Freundlich isotherms. AL-Aoh et al. [20], in their study, examined the removal of 4-nitrophenol by palm kernel shell-based activated carbon, coconut shell-based activated carbon and coal-based activated carbon by adsorption method. It was stated that all three adsorbents were compatible with both Freundlich and Langmuir adsorption models. Sreelatha et al. [11], in their study, examined the adsorption efficiency of textile dye by subjecting a protein-based substance called chitin, which is found on some crustaceans and called "Chitosan", to acid treatment with the powdered form of palm kernel shell-based activated carbon from textile industry wastewater. They investigated its compliance with the Freundlich and Langmuir adsorption models. It was stated that it was compatible with both

Freundlich and Langmuir adsorption models. Onundi et al. [12] reported that the Langmuir adsorption isotherm was more compatible than the Freundlich isotherm model in their study on the removal of copper, nickel and lead from wastewaters by adsorption with palm kernel shell-based activated carbon. Pan et al. [21] examined phenol removal from aqueous solutions with porous acrylic ester polymer (Amberlit XAD-7) as adsorbent. It was observed that suitable phenol adsorption was at acidic solution pH, and the increase in solution pH resulted in a significant decrease in adsorption capacity. It was found that adsorption was compatible with both Langmuir and Freundlich isotherms, and the adsorption capacity was stated as 100 mg.g⁻¹.

If $n=1$ in isotherm models, adsorption is linear. This indicates that adsorption sites are at homogeneous energy (as in the Langmuir model) and that there is no interaction between the adsorbed species. If $1/n < 1$, adsorption is suitable, adsorption capacity increases and new adsorption sites are formed. If $1/n > 1$, adsorption bonds are weakened and unsuitable adsorption occurs, resulting in a decrease in adsorption capacity.

For palm kernel shell-based activated carbon, $1/n < 1$ was found in the Freundlich adsorption isotherm model. The found values overlap with the data. It is concluded that palm kernel shell-based activated carbon is a good adsorbent for paper wastewater and can be used as an alternative.

4. CONCLUSIONS AND RECOMMENDATIONS

In the thesis study, phenol adsorption, which shows toxic effects, from paper industry wastewaters was investigated using palm kernel shell-based activated carbon (PKAK) as an adsorbent. The studies showed that contact time, adsorbent amount and pH were effective in the adsorption capacity of the adsorbent.

As a result of the studies conducted to determine the contact time, it was determined that the maximum adsorbent capacity for PKAK was reached in 60 minutes. The maximum adsorption capacity at equilibrium time is 200 mg/g.

In the experiments conducted to determine the effect of pH, when the pH value changed from 2 to 12, the adsorption capacities changed from 186.66 mg/g to 143.33 mg/g, respectively. The pH 6-9 range was found suitable for pH discharge standards in the Water Pollution and Control Regulation for paper industry wastewater. The pH value of the paper wastewater used in the analyses is 6, which is suitable for discharge criteria. It is considered appropriate to increase the phenol removal efficiency by keeping the paper wastewater in the desired pH range of 6-9 and applying other conditions (adsorbent amount, contact time and temperature) at the optimum level. There are also studies in the literature that support this information.

In the studies to determine the optimum adsorbent amount, it was observed that the amount of phenol remaining in the solution after adsorption decreased as the adsorbent amount increased. When the adsorbent amount was increased from 3 g/L to 20 g/L, the equilibrium adsorption amount, q_e , decreased from 203.33 mg/g to 24 mg/g. It is seen that the q_e value is 203.33 mg/g when the adsorbent amount is 3 g/L. For this reason, the optimum adsorbent amount was accepted as 3 g/L. In addition, it was observed that filter clogging and interference in experiments occurred at higher adsorbent amounts.

In the studies conducted to determine the adsorption kinetics, the results of linear regression analyses were investigated. Experiments were conducted at values between 20-40 °C to investigate the effect of different initial temperatures on adsorption. While phenol adsorption increased from 20 °C to 30 °C, it decreased at 35 °C and 40 °C. The highest experimental q_e values were obtained at 30 °C. It is thought that the reason for this may be the weakening of the interaction between the adsorbent surface and phenol components and the decrease in adsorption as a result of the increase in temperature. In the kinetic study of phenol removal with palm kernel shell-based activated carbon, it is seen that the pseudo-first-order reaction kinetics fits better than the pseudo-second-order reaction kinetic model.

The correlation coefficients (R^2) obtained as a result of applying Freundlich and Langmuir isotherms revealed that PKAK and phenol adsorption were compatible with both isotherms. As a result of the K and q_m constants obtained by calculation, we can say that the affinity between the adsorbent and phenol components is high and that palm kernel shell-based activated carbon can be a good adsorbent for phenol removal by adsorption method in paper wastewater. Studies on palm kernel

shell-based activated carbon in the literature support this information. For palm kernel shell-based activated carbon, $1/n < 1$ was found in the Freundlich adsorption isotherm model. The found values overlap with the data.

It is thought that palm kernel shell-based activated carbon can be used as an alternative adsorbent because it is a vegetable by-product with a wide pore structure, high acidity ratio, high binding property, easily accessible and cheap. It has been determined that it is a good adsorbent with 70.58% phenol removal efficiency under optimum conditions in paper wastewaters, which are difficult to treat.

Perrich [22] determined in his study that activated carbon, which is frequently used in adsorption processes, has a very large surface area thanks to its extremely complex network-shaped pores, and therefore, although it is very effective in the adsorption of phenol and phenol derivatives, its regeneration is a difficult and expensive method. For all these reasons, it is thought that palm, which is a fire-resistant tree species that has been grown more in our country recently, can be used as a good activated carbon material.

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